Co-Pyrolysis and Synergistic Effect Analysis of Biomass Sawdust and Polystyrene Mixtures for Production of High-quality Bio-oils

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ABSTRACT

Usage of traditional biomass raises serious concerns regarding its sustainability due to the inefficient combustion in household stoves and potential over-usage if the intention is to replace fossil fuels in power plants. Co-pyrolysis of biomass feedstock with different waste materials, especially plastics, might be a promising alternative for sustainable usage of enhanced biofuels. Even more, co-pyrolysis can help to integrate waste management schemes into the power production sector. Plastics materials have properties similar to those of fossil fuels in terms of heating value and the absence of oxygenated compounds; therefore, they could significantly improve the properties of biomass products, especially bio-oils. Especially interesting for this method is polystyrene (PS) since it yields a high share of liquid fraction, which is the most valuable pyrolytic product. In this work, co-pyrolysis was performed for a mixture of waste biomass sawdust (oak, poplar and fir wood) and waste polystyrene from dairy product packaging. Pyrolysis was carried out for biomass and polystyrene alone, and their respective fuel blends (PS/SD 25-75%, PS/SD 50-50%, PS/SD 75-25%) from room temperature to 600°C with a retention time of half an hour. The highest yield of liquid fraction was noticed for mixtures with 75% of PS, while the lowest one was for blends with 25% of PS, with a yield of 83.86% and 62.33%, respectively. Additionally, the mass spectrometric analysis was carried out to determine the chemical composition of the obtained oil.

1. INTRODUCTION

High reliance on fossil fuels as a primary energy source raises serious environmental and social concerns, due to increased pollution and a strong impact on climate changes. Even though it is expected that electrification will significantly contribute to decarbonisation of all sectors, additional high-energy-density alternative fuels are inevitable [1]. This is due to the fact that electrification of high-temperature processes [2] or long-range voyages might not be efficient and practical [3]. Biomass and biofuels are already used as an alternative energy source in various applications, even though their consumption and usage in poorly efficient stoves with low efficiency is not sustainable and should be avoided in future [4]. Liquid biofuels, which are already deployed on a commercial scale, have serious drawbacks like low heating value, a high share of oxygenated compounds (35-60%), poor thermal stability, higher viscosity and acidity [5]. To enhance biofuels properties, different thermochemical methods like pyrolysis [6], gasification [7], and anaerobic digestion [8] are lately promoted as a potential solution. Pyrolysis is especially interesting since it can simultaneously enhance the properties of all obtained pyrolysis fractions (liquid, gas, solid). The main product obtained from pyrolysis is bio-oil which also has the greatest commercial potential to be further refined into biodiesel and used in fuel blends with gasoline [9]. Since the pyrolysis itself can partially prevail the drawbacks mentioned above, co-pyrolysis with waste materials, especially plastics, was introduced [10]. About 27 million tons of plastic waste is generated in EU in 2018 of which 31.1% is recycled, 41.6% is used for energy recovery while the rest is landfilled which presents a serious environmental problem, but also the irrevocable loss of valuable resources [11]. The oil obtained from plastic pyrolysis have some good characteristics similar to conventional gasoline, like high heating value and hydrocarbon content [12]. Nevertheless, in such oils higher share of harmful compounds like polycyclic aromatic hydrocarbons (PAHs), furans, dioxins, benzenes and similar is present, which constrains wider application or requires complicated and expensive after-treatment [13]. Co-pyrolysis looks like a promising solution since it can process waste materials and convert them into highly valuable fuels or chemicals [14]. In such a process, plastics are used as some form of catalyst to improve the yield of aromatic hydrocarbons and decrease the share of oxygenated compounds in the liquid fraction. Therefore, utilisation of waste biomass (sawdust, wood chips, branches) and end-of-life plastics might be a great solution to tackle multiple challenges [15]. Produced alternative fuels can be utilised where appropriate; waste management could be efficiently integrated with the energy sector, while biomass consumption can be maintained at sustainable levels since the need for feedstock is partially satisfied with waste plastics.

Up to know, significant research efforts are given to find the optimal conditions and bring the process on a larger scale. Abnisa et al. [14] provide a review on the co-pyrolysis process regarding the feedstock selection, process parameters, decomposition mechanisms and product yield. Additionally, the study gives a comprehensive review of the characteristics of common waste plastic materials with their Ultimate and Proximate analysis, and potential utilisation as a pyrolysis feedstock. Uzoejinwa et al. gave an in-depth review with achieved accomplishments in field and prospectives for future work [16]. In this work, main products of thermal decomposition of various biomass and plastic materials are given, alongside their main degradation mechanism. Even more, the author's present a very detailed review regarding the synergistic effect that occurs between investigated feedstock, as well as their possible reaction mechanisms. As a prospect for future work and directions, the authors suggest the usage of an acidic catalyst to enhance the selectivity of products, but also the usage of microalgae and seaweed biomass as a feedstock. Yang et al. [17] investigated the fast co-pyrolysis of low-density polyethene (LDPE) with three different biomass feedstock. In this study, the detailed analysis is given regarding the oil characterisation, and it is concluded that co-pyrolysis enhances the yield of hydrocarbons through the synergistic effect. Hassan et al. [5] provide a good insight on recent progress on biomass co-pyrolysis for bio-oil production, including both catalytic and non-catalytic. Hassan et al. [18] analysed the aromatic hydrocarbon yield from fast co-pyrolysis of torrefied biomass and polystyrene (PS). This study shows that co-pyrolysis can significantly enhance the yield of aromatics while decreasing the content of oxygenated compounds. Moreover, in this study, a potential mechanism for the formation of major aromatic hydrocarbons is given. Ozsin and Putun [19] presents a comparative study on the co-pyrolysis of biomass with different plastics. The study concludes that the synergistic effect and product yield, besides process parameters, depends on biomass-plastic feedstock ratio in the fuel blend. Nevertheless, all mixtures express the reduction of oxygenated compounds and increment in heating value. Ephraim et al. [20] analysed the synergistic effect and product yield for various plastic materials. Even though all investigated samples showed synergy, opposite trends are noticed, which implies that product yield depends on feedstock selection. Finally, various kinetic analyses are performed to investigate the influence of different atmospheric conditions [21], and catalytic effect on product yield [22]. Especially interesting is the co-pyrolysis of biomass with waste PS, which yields a high share of liquids with aromatic hydrocarbons required to meet fuel specifications [23]. Since some form of waste PS materials are inappropriate for conventional recycling methods or are not even included in plastic recycling schemes, this marks them as an ideal feedstock for co-pyrolysis.

In this study, biomass sawdust is co-pyrolysed with waste PS, with an aim to investigate the influence of plastic content on bio-oil properties. Up to know, process parameters and their influence on product yield were widely investigated, while more needs to be done regarding the feedstock selection. The main objective of this study is to analyse the influence of plastic content on bio-oil quality by evaluating the level of synergy between feedstock and observing the composition of bio-oils derived from mixture co-pyrolysis. Even though the introduction of plastic content enhances the bio-oil properties, it was noticed that after some point, a further increment of plastic share in the mixture has more negative impact promoting the formation of unwanted compounds. Therefore, determination of the optimal mixing ratio is important to produce high-quality biofuels, but even more, to reduce the need for expensive after-treatment methods.

2. MATERIALS AND METHODS

2.1. Material characterisation

Samples investigated in this study were waste plastic and biomass materials. The plastic feedstock was waste polystyrene (PS) previously used as a packaging material for dairy products, while biomass was obtained from a local sawmill in the form of sawdust (SD) mixture of beech, oak and fir with the unknown shares. Prior to experimental investigations, sample preparation was carried out by shredding, grinding and sieving into finer particles (0.125-0.25 mm) to obtain homogenous fractions. Materials were obtained with unknown chemical and elemental composition. The elemental characterisation was carried out by the FlashSmart Analyzer on about 2 mg of a sample, and the results are given in Table 1.

Table 1. - Ultimate analysis of polystyrene and sawdust samples

	C (%)	H (%)	N (%)	O (%)	Ash (%)
PS	89.58	8.22	-	0.92	1.28
Sawdust	46.49	6.03	2.47	44.51	0.50

2.2. Thermal decomposition investigation

To determine optimal co-pyrolysis conditions, thermogravimetric analysis (TGA) was carried using TGA/DSC 2 Thermoanalyzer Mettler Toledo. Samples were investigated individually and in mixtures with different shares: PS/SD 25-75%, PS/SD 50-50%, PS/SD 75-25%. Samples of about 10 mg were heated in Al_2O_3 crucibles of 70 µl, from room temperature to 600°C, at a heating rate of 10 °C/min. As a carrier gas nitrogen was used with a flow rate of 20 ml/min. Samples were held at the final temperature for 30 min.

2.3. Pyrolysis conditions and product analysis

The pyrolysis experiments were performed in a stainless-steel fixed bed reactor. The temperature of the reactor was controlled by a PID temperature controller (Model 4836, Parr), whereas a K-type thermocouple sensed the temperature of the reaction. A more detailed description of the reaction set-up has been described by Hlavsová et al. [24]. The experiments were carried out under a nitrogen atmosphere with a flow rate of 80 ml/min. Approximately 2 g of the sample was placed in the reactor and heated at 10 °C/min to a final temperature of 600 °C. The final temperature was maintained for about 30 min or until the complete release of pyrolysis gases. Samples were pyrolysed individually and in respective mixtures. The yield of the solid fraction was calculated by weighing the sample mass before and the residual mass after the pyrolysis. The yield of pyrolysis gas was calculated at N_2 free-vol.%, and it is based on the volume fractions obtained from gas chromatography (GC) and densities of individual gas components. Condensable gases were cooled down using an ice bath and collected in liquid form at the end of a reactor. Share of liquid fraction was calculated by the difference. The experiments were duplicated to validate the results.

The pyrolysis liquids were diluted 1:10 by dichloromethane. An internal standard of 1,3,5-tri-tert. butylbenzene (100 ng/µl, Merck) was added. Composition analysis was done by GC/MS (Agilent 7890, 5975 C). About 1µl aliquot of sample was injected in split ratio 1:10 by MultiPurpose Sampler (MPS, Gerstel, Muelheim an der Ruhr) into Agilent 7890 A equipped with a HP 5 ms column (60 m x 0,25 mm x 0,25 µm, Agilent J&W). The injector temperature was set at 250°C. Helium was used as carrier gas at a constant flow rate 1ml/min. The organic compounds were separated (on column) by the following programme: 48°C (retention time 2.5 min.) to 280°C (hold time 0.5 min.) with a rate 5°C/min. The transfer line temperature was set at 280°C, quadrupole and ion-source temperature 150 and 230°C. The mass spectrometric analysis was performed in the range of m/z=35-650. The identification and quantification of the individual organic compounds were carried out by standards and programs Agilent Qualitative and Unknown analysis. Figure 1 presents the experimental setup used in this study for the co-pyrolysis, while it can also be used for gasification. The similar setup, with only few modifications, was also used by Hlavsova et al. [24] where syngas production was studied from the pyrolysis of various Perennial grasses.

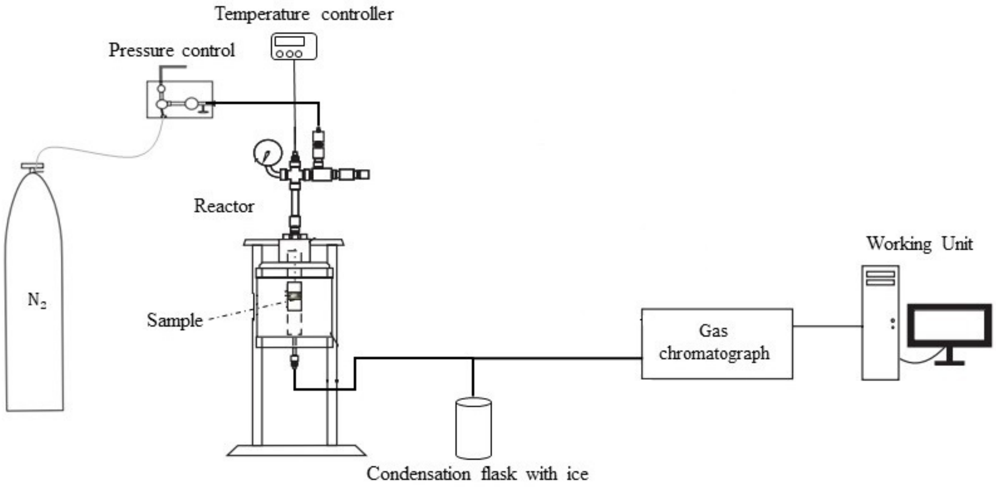
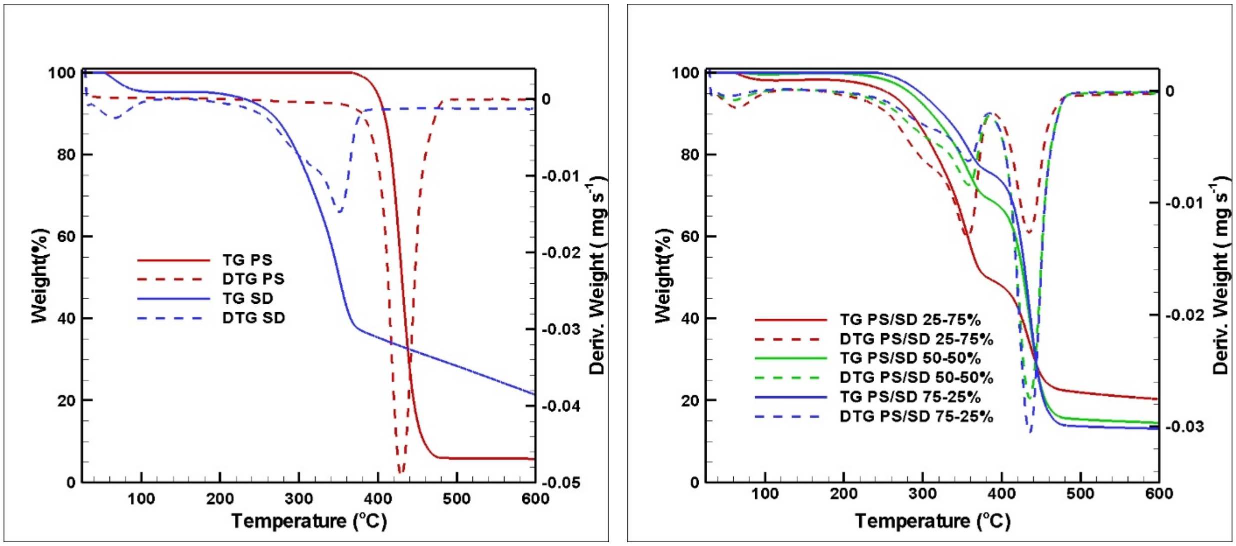


Figure 1 – Experimental setup used for the pyrolysis and co-pyrolysis of investigated samples

3. RESULTS

3.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an important technique used to determine the thermal decomposition mechanism of investigated feedstock [25]. The TGA is especially important to determine optimal operating co-pyrolysis conditions, especially when samples have a different origin, composition and thermal stability. Figure 2. presents the thermogravimetric (TG) curves for individual samples (a) and corresponding mixtures (b). As it can be seen (Fig. 2a) thermal decomposition of PS consists of one step between 367°C and 482°C, with a peak at 425°C. When the temperature reaches 600°C, solid residue is about 5.67%, additionally lowered to ~5% after 30 min of retention time. Similar results are already reported in the literature [26]. Thermal decomposition of biomass sawdust consists of three stages, starting at around 50°C with the dehydration up to 200°C, where approximately 5% of mass loss is noticed. The second stage, between 200 and 370°C, presents the most intensive decomposition with a peak at around 350°C, where mostly cellulose and hemicellulose, is decomposed [27]. In this stage, the mass of the sample is more than halved to approximately 37%. The last stage follows a linear trend, and when the temperature reaches 600°C biochar mass is about 21%. After a retention time of 30 min, the final mass is slightly below 10% of initial weight, indicating higher lignin and mineral content in the investigated sample [28].



a) b)

Figure 2. - TG curves for individual biomass and PS samples (a) and their respective mixtures (b)

Obtained TG curves for polystyrene and sawdust mixtures (Fig. 2b) shows an obvious synergy compared to the individual analysis. All blends express three stages of decomposition, starting with the evaporation at around 65°C up to 100°C. For the mixture with a low share of PS, the evaporation stage is not notably affected. With the gradual increase of the PS content, the onset temperature for moisture evaporation for SD is decreased from 65°C to 58°C for the mixture with 50% of PS, and to 53°C for the mixture with 75% of PS. This implies that plastic content affects the moisture evaporation of the biomass component by lowering the onset temperature. In addition, PS reduced the intensity of evaporation, and as it can be seen from Figure 2b), only the mixture where SD is a dominant component has a visible mass loss. Similar to individual TGA of SD, second stage decomposition starts slightly below 200°C, and goes up to 380°C, with a peak at 360°C. In this stage, the introduction of PS broadens the temperature range in which conversion is happening by lowering the initial temperature, simultaneously increasing the final stage temperature. The highest mass loss is noticed for the mixture with 75% of SD, which suggests that the biomass components (cellulose and hemicellulose) play an important role in this temperature range. The last stage of decomposition starts at around 400°C, and it goes up to 480°C, after which the mass loss is almost negligible. It is interesting to notice that the mixture with 75% of SD has the lowest conversion in this stage, which implies that biomass decomposition is dominant for mild temperatures [29]. Blend with the 75% of PS, expressed the most intense degradation in the third stage, which is expected since that individual TGA showed that in this temperature range PS decompose rapidly. Mixture with an equal share of both feedstocks shows similar behaviour to those where PS is dominant. Table 2. presents the initial and final mass for investigated samples.

Table 2. - Initial and final mass of investigated samples

Sample	Initial mass [mg]	Final mass [mg]
Sawdust	10.602	1.048
PS	10.935	0.616
PS/SD 25-75%	11.667	2.193
PS/SD 50-50%	12.139	1.654
PS/SD 75-25%	11.161	1.367

3.2. Pyrolysis product analysis

3.2.1. Product yield

Before being introduced to co-pyrolysis, PS and SD were pyrolysed individually to obtain referent values and calculate the theoretical yield of pyrolytic products. Theoretical yield is then compared with experimentally obtained values to determine the level of synergy between investigated feedstock. Fig 3. presents experimentally obtained values for all investigated samples. As expected, the dominant fraction from the pyrolysis of PS is liquid with a yield of 96.02%, while the share of a gas fraction is almost negligible (<1%). Previous investigations show the yield of liquid fraction between 80-90% [21, 24, 25], while Ephraim et al. [20] reported the yield higher than 99%. On the other hand, the main products from the SD pyrolysis are gases (48.10%), followed by liquid and char with a yield of 31.39% and 20.51%, respectively. Nguyen et al. [32] pyrolysed the pine sawdust, where product distribution was following; 48.83% of bio-oil, 31.29% of char, and 19.88% of gases. It can be seen that even though the product shares are similar, the distribution is entirely different. This is due to the fact that product distribution from biomass pyrolysis is strongly influenced by the content of cellulose, hemicellulose and lignin [33]. Higher lignin share indicates higher char yield, while the cellulose component promotes the yield of liquids and gases. Biomass is also characterised by a higher share of fixed carbon and ash content which favours char yields [34], while plastics have a high share of volatiles (>90%) which promotes liquid yield. Therefore, if there is a synergy in the co-pyrolysis process, it is expected that obtained values from investigated mixtures will be between these obtained from individual pyrolysis.

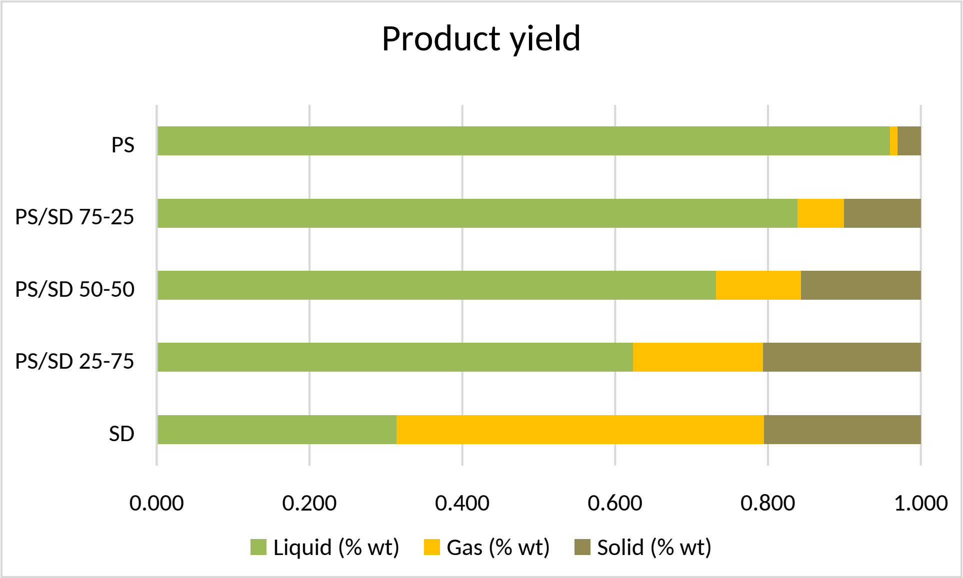


Figure 3. - Product yield from individual pyrolysis and PS/SD blends co-pyrolysis

From the co-pyrolysis, the highest liquid (oil) yield (83.86%) is noticed for the mixture where PS is dominant in the blend, while the lowest yield (62.32%) is obtained for the blend where SD is a major component. The yield of gas and solid fractions shows the opposite behaviour, and the highest yield is noticed for the mixture with 75% of SD where the yields are 17.01% and 20.66%, respectively. Mixture with an equal share of PS and sawdust, yield the values which are in between of these obtained from the co-pyrolysis of blends where a dominant component is either PS or SD. In Figure 2 it is interesting to notice how the increment of PS content promotes the yield of liquids, simultaneously decreasing the share of gas and solid products, which suggest that synergistic effect is achieved in the process [35]. Even more, it should be emphasised that the addition of only 25% of PS to the mixture, completely changed the product distribution compared to the individual biomass pyrolysis. Even though the gases are main products of biomass pyrolysis, 25% of PS in fuel mixture doubled the liquid yield completely on the expense of gas generation. The share of char is not significantly affected, which is expected since the PS decomposition yields an almost negligible amount of solid residue due to high volatile content. This suggests that PS could be effectively used with different types of biomass to improve the oil yield information could be especially important for the pyrolysis of sawdust mixtures, where often precise composition and content of major biomass components is not known. More on this will be discussed in the following subsection.

3.2.2. Synergistic effect

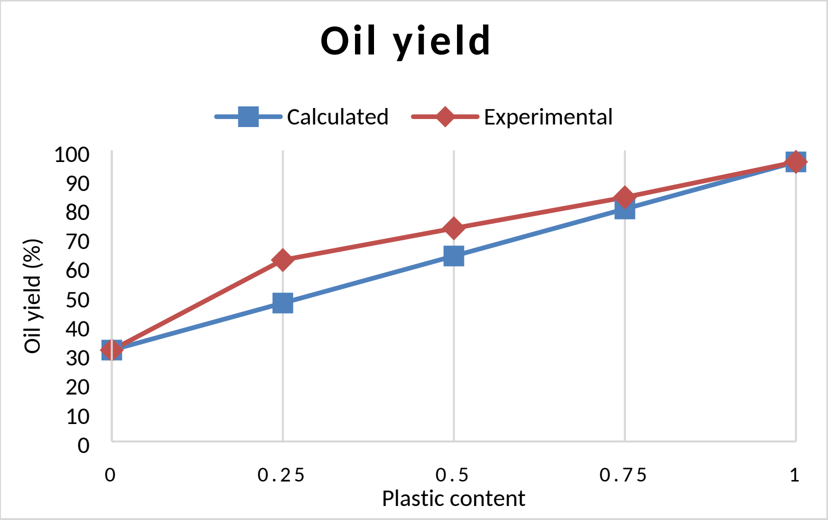
To determine the level of synergy, experimental results are compared to the theoretical values. Theoretical values (Y_{cal}) are calculated using the following equation (1):

$$Y_{cal}=W_{SD}Y_{SD}+W_{PS}Y_{PS} \quad (1)$$

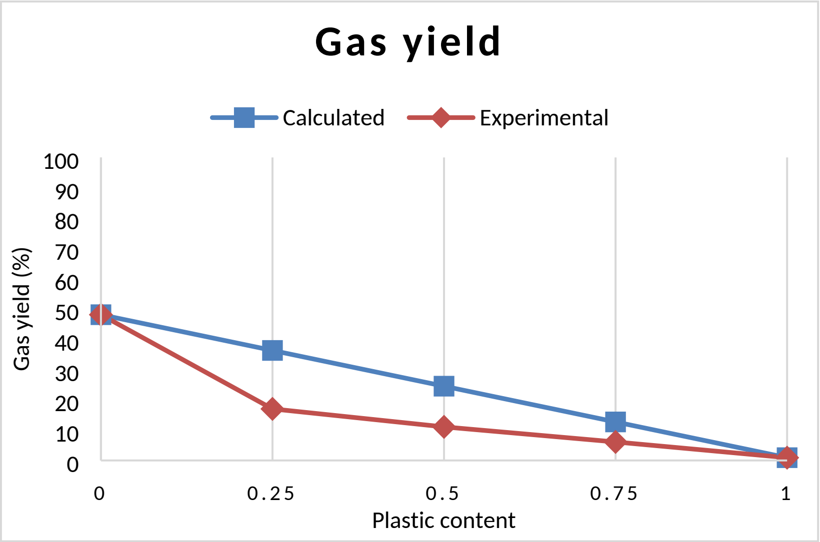
Where $W_{SD/PS}$ stands for proportions of each component in investigated mixtures, and $Y_{SD/PS}$ presents the values obtained from the individual pyrolysis [20]. Existence and level of synergy are determined by the difference between experimentally obtained values and calculated ones using equation (2). According to Hassan et al. [5], it can be stated that synergy exists when the difference between the experimental and calculated values are positive.

$$\Delta Y = Y_{exp} - Y_{cal} \tag{2}$$

Figure 4. presents the charts with the calculated theoretical and experimentally obtained values for liquid (a), gas (b) and char (c) products. As can be seen, the most significant synergy is achieved for a liquid fraction (Fig 4a), especially for the mixture with 25% of PS. As the content of PS increase, synergy is still evident but with lower intensity, which is expected since the experimental values are approaching theoretical [23]. The same is noticed for the char yield (Fig. 4b), where the mixture with the 25% of PS shows the highest synergy effect, which decreases as the PS content increase. Nevertheless, strong negative synergy is observed for gas yield (Fig. 4c). This indicates that interaction between PS and SD promotes the yield of oil and char, on the expense of gas generation. It is interesting to notice that in literature, positive values for char are almost always reported [14], while the synergy for oil and gas yield strongly depends on feedstock selection and process conditions. High heating rates, temperatures and longer residence time will promote the formation of gaseous compounds [20] as the products of secondary oil cracking [28], [36].



a)



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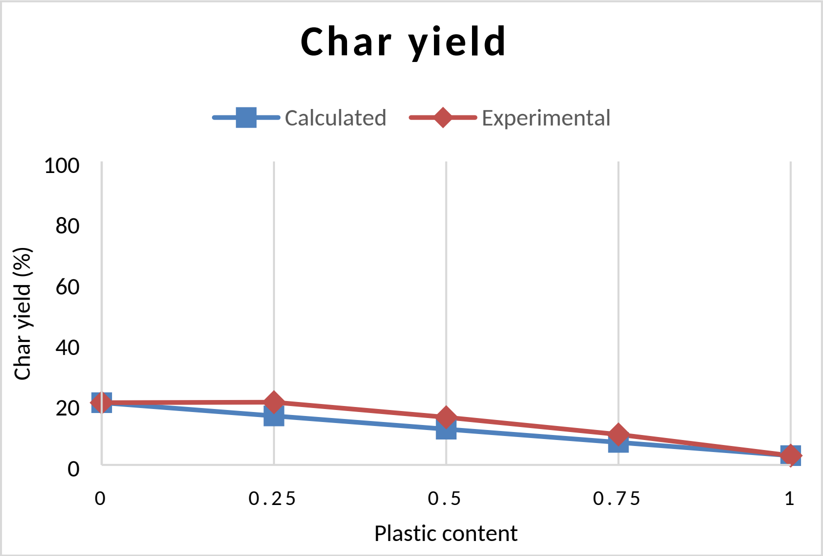


c)

Figure 4. - Evaluation of synergistic effect for each fraction yield

Detailed values regarding each fraction yield from investigated blends are presented in Table 3., alongside the calculated level of synergy. For the pyrolysis of pure PS and SD theoretical values are equal to experimental (Exp.), since they represent the maximum yield of products for investigated samples. Therefore, the level of synergy ΔY is equal to zero.

Table 3. - Theoretical and experimental values for product yield and calculated level of synergy

Sample	**Liquid fraction**			**Gas fraction**			**Solid fraction**		
	Theoretical	**Exp.**	**ΔY**	**Theoretical**	**Exp.**	**ΔY**	**Theoretical**	**Exp.**	**ΔY**
PS	96.02	96.02	0	0.92	0.92	0	3.06	3.06	0
Sawdust	31.39	31.39	0	48.10	48.10	0	20.51	20.51	0
PS/SD 25-75%	47.55	62.32	14.77	36.31	17.01	-19.29	16.15	20.66	4.52
PS/SD 50-50%	63.71	73.22	9.52	24.51	11.08	-13.43	11.78	15.70	3.91
PS/SD 75-25%	79.86	83.86	4.00	12.71	6.10	-6.61	7.42	10.03	2.61

Comparing to the investigation carried out by Ephraim et al. [20] where poplar wood was co-pyrolysed with PS at 750°C, a higher level of synergy is achieved for all investigated mixtures. In addition, Ephraim et al. [20] noticed negative synergy for oil yield and positive synergy for gas yield, probably due to the higher reactor temperature. Even though strong negative synergy is visible for gas yield in this study, the total yield is still higher compared to the mentioned study. Since the different type of biomass feedstock is used in these two studies, this indicates that biomass feedstock plays a dominant role for product distribution, while PS is responsible for maximizing the oil yield on the expense of gaseous and solid fraction [37]. The investigation carried out by Reshad et al. [28] where rubber seed cake was investigated with waste PS at 500°C presents results that confirm the above-stated statement.

3.2.3. Liquid products characterisation

The liquid fraction obtained from co-pyrolysis is the most abundant, and the most valuable in terms of potential commercial utilisation [38]. Firstly, pyrolysis was performed solely for SD to obtain a liquid fraction that represents a referent case of bio-oil. Altogether, obtained bio-oil is composed of 90 different organic compounds, while only 43 of them are present with a notable share of at least 1%, which was chosen as a threshold for further analysis. Selected compounds represent about 80% of the bio-oil composition, and most of them can be considered oxygenated with at least one oxygen atom. Only non-oxygenated compounds found are styrene, toluene and polycyclic aromatic hydrocarbons (PAHs) which combined accounts for about 13% of oil composition. Compounds with the highest yield are listed in Table 4. In general, bio-oil has a heterogeneous structure with a wide variety of identified compounds where most of them are present in traces or with meagre share [39].

Table 4.- Most significant compounds identified in bio-oil

Compound	**Share [%]**
1,6-Anhydro-b-D-glucopyranose (levoglucosan)	2.09
2,6-Dimethoxytoluene	2.14
2-Methoxyphenol	2.74
2-Pentanone	2.59
4-Methoxyphenol	2.39
Acetophenone	5.86
Dodecanoic acid	2.19
Furfural	5.81

Naphthalene	1.85
Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	6.82
Propanone	2.05
Styrene	1.90
Toluene	2.93
Vanillin	2.92
Sum of selected compounds	**42.39**
Compounds with a share below 1.0%	**37.43**

On the other hand, oil derived from the PS pyrolysis is composed mostly of aromatic and polycyclic aromatic hydrocarbons. Even though altogether 89 various organic compounds are identified, only 20 of them are represented in notable share (>0.50%), and they account for ~90% of all identified compounds. Moreover, the nine selected compounds which are given in Table 5. account for about 82% of all identified compounds which implies that liquid fraction derived from the pyrolysis of PS have more homogenous composition then bio-oil, even though the total number of identified compounds is similar. Most probably, this is due to simple PS composition which primarily decomposes on monomer styrene, compared to complex biomass decomposition which undergoes through various dehydration, decarbonylating, and decarboxylation reactions [40]. Results obtained for PS oil are similar to those found in the literature regarding the yield of major compounds [31]. Nevertheless, the lower yield is noticed for ethylbenzene, while there is a complete absence of toluene. Moreover, Cyclohexane, 1,3,5-triphenyl-, which is classified as PS impurity, is identified with a significant share, which was not previously reported in the literature. In general, a relatively lower share of monomer styrene, and a pronouncedly higher share of styrene derivatives, suggests that longer retention time and lower heating rates promote the secondary cracking reactions and formation of various aromatic hydrocarbons [41].

Table 5.- Most significant compounds identified in PS oil

Compound	**Share [%]**
α-Methylstilbene	7.11
α-Methylstyrene	10.95
1-(4-Methylphenyl)-4-phenylbuta-1,3-diene	1.66
1,2-Diphenylcyclopropane	3.52
1,3,5,7-Cyclooctatetraene	4.57
Benzene, 1,1'-(1,3-propanediyl) bis-	6.24
Cyclohexane, 1,3,5-triphenyl-	17.71
Ethylbenzene	4.84
Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	10.77
Styrene	16.47
Sum of selected compounds	**82.19**
Compounds with a share below 0.5%	**17.81**

Chemical characterisation of derived oil from the co-pyrolysis of PS/SD blends is one of the main objectives of this study. For all investigated blends, it was noticed the increase of the total number of derived compounds from 90, for individual pyrolysis, to more than 120 from co-pyrolysis. Detailed analysis showed that the dominant compound found in derived oils are those which are also found in PS oil, indicating that plastic material is dominant for the yield of liquid products [42]. Table 6. presents the yield of selected compounds and their respective share. It is interesting to observe that the increment of PS in the mixture decrease the yield of styrene and promote the yield of toluene, suggesting that SD influences the secondary cracking of monomer styrene. This is also confirmed by the high yield of monomer styrene (27.38%) for mixture with 25% of PS. Moreover, it is interesting to compare the yield of Naphthalene, 1,2,3,4-tetrahydro-2-phenyl- identified in bio-oil, as well as the PS oil. Mixture with 25% of PS expressed a great reduction in yield of this PAH compared to individual pyrolysis. Further increment of PS content promotes the higher yield of this compound, with the maximum share of 8.73% for a mixture where PS is dominant, which is still lower compared to the individual pyrolysis of PS. Since there is no obvious increase in the yield of other PAHs, it can be stated that SD hinders the formation of these harmful compounds, as a positive outcome of feedstock interaction. In addition, the increase of PS in the mixture decreases the yield of Cyclohexane, 1,3,5-triphenyl-**.** This phenomenon is interesting since the Cyclohexane, 1,3,5-triphenyl- is PS derivative product; thus it is expected that its yield would increase with the increment of PS content. It is also interesting to observe the yield of toluene which increases with the increment of plastic content, even though this compound was not found in PS oil. Toulene is a product of secondary cracking of styrene monomer which is obviously encouraged by the feedstock interaction in the co-pyrolysis [30]. Finally, it should be noted that increment of PS in fuel mixtures promotes the formation of benzene-based compounds, which could constrain further utilisation of obtained oils since such compounds are classified as carcinogenic.

Table 6. - The yield of selected compounds in investigated mixtures

Compound	**PS/SD 25-75%**	**PS/SD 50-50%**	**PS/SD 75-25%**
	Share [%]	Share [%]	Share [%]
α-Methylstyrene	4.82	7.69	8.33
1,2-Diphenylcyclopropane	2.24	3.23	4.04
Benzene, 1,1'-(1,3-propanediyl) bis-	3.65	6.46	7.98
benzene, 1,1',1''-[5-methyl-1-pentene-1,3,5-triyl] tris-	5.10	0.90	0.61
Cyclohexane, 1,3,5-triphenyl-	19.97	8.99	11.70
Cyclopentane, methyl-	3.44	1.18	0.73
Ethylbenzene	7.25	11.28	8.76
Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	5.95	7.32	8.73
Styrene	27.38	23.40	15.21
Toluene	1.12	5.70	8.15
Sum of selected compounds	**80.91**	**76.15**	**74.25**
Compounds with share below 0.5%	**19.09**	**23.85**	**25.75**

One of the biggest drawbacks for the bio-oil utilisation is the high share of oxygenated compounds, which results with reduced heating value and poor thermal stability [43]. Introduction of PS is expected to reduce the yield of such compounds and instead, promote the formation of hydrocarbons. Table 7. summarised selected organic groups and compounds which are found in investigated oils. An additional comparison is carried out regarding the C-content range of identified organic compounds. The division is made between gasoline-like (C_4-C_{12}) and jet-fuel (C_8-C_{16}) compounds [36].

Obtained bio-oil has a significant number of oxygenated compounds like phenols, ketones, aldehydes, ethers, acids, and a notable amount of sugars and alcohols. Besides, a pronouncedly high share of PAHs and furans is identified, slightly below 12%. In general, bio-oil is composed of gasoline range compounds C_{4-12} (69.10%), while major compounds found in PS oil are high aromatic hydrocarbons (79.33%), which would fit jet fuel requirements regarding the C-content. Even though aromatics have great calorific value, their combustion releases a large amount of smoke and harmful species, raising serious environmental and health concerns. For this reason, their share in fuel composition is restricted to 40% for gasoline fuels, 25% in the case of JP-4, and only 5% for JP-7 fuels [44]. Surprisingly, almost the same share of PAHs (12.14%) is identified in PS oil and bio-oil. Analysis of oil obtained from co-pyrolysis express expected behaviour in terms of decreasing the oxygen-containing compounds and increment of hydrocarbon content [23]. Nevertheless, only 25% of PS in the blend, almost completely reduce the content of oxygenated compounds, simultaneously increasing the share of higher hydrocarbons. Of all identified organic groups in bio-oil, only Phenols remained with a notable yield of 3.72%, while the rest are present in traces. In addition, blend with 25% of PS showed the most significant reduction in terms of PAHs content, from almost 12% for individual pyrolysis to 6.86%. The yield of PAHs is especially interesting. While the individual pyrolysis yields a high share of such compounds, investigated mixtures expressed notable reduction, especially for these with lower plastic content. Increment of PS content in investigated blend leads to further decrease of oxygenated species; nevertheless, higher generation of PAHs is noticed. This indicates that the optimal mixture ratio might promote the interaction between feedstock, which hinders the cumulative yield of PAHs found in oil from individual pyrolysis [45].

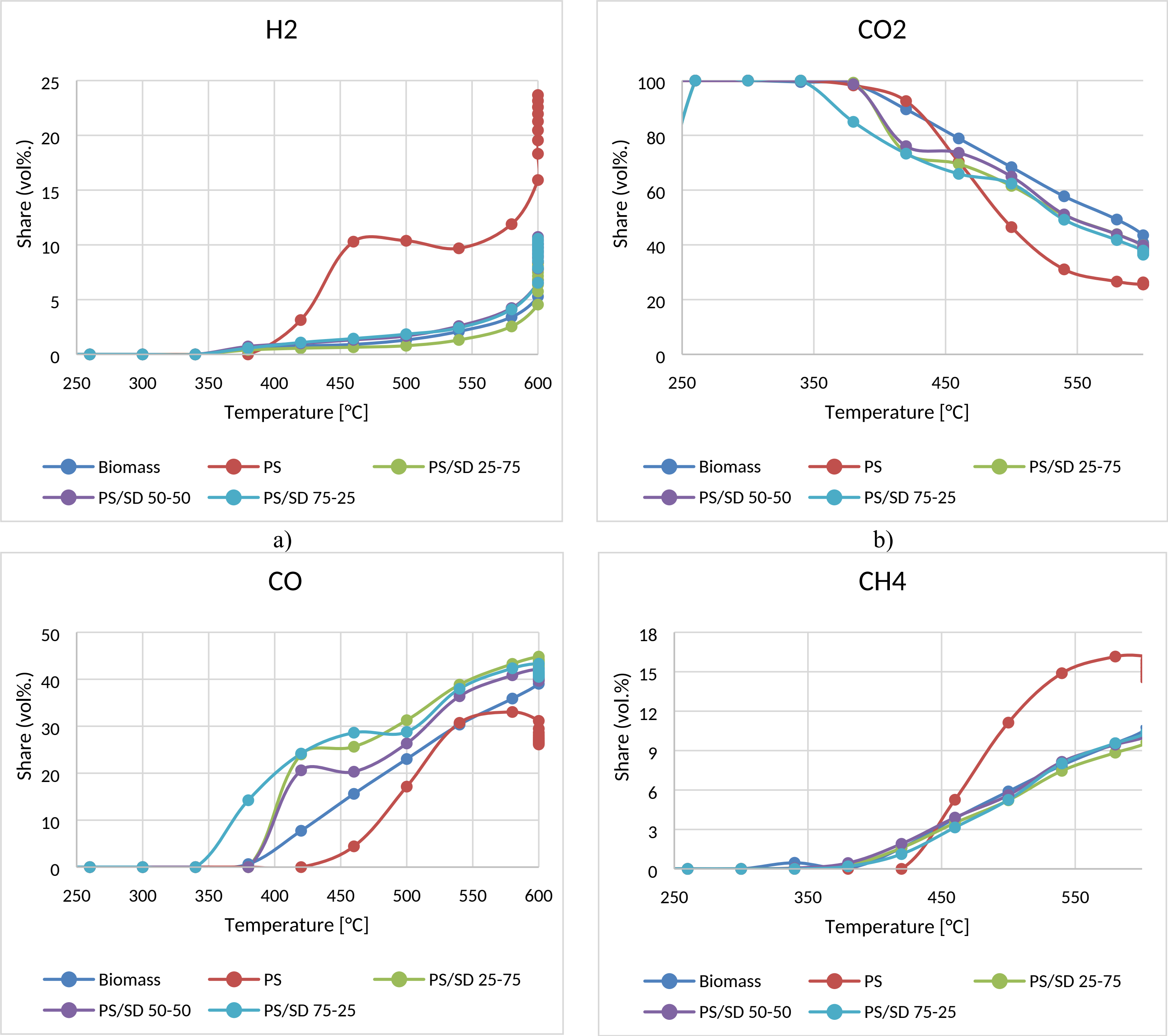
Majority of identified compounds in bio-oil are in the range of gasoline-like compounds regarding the C-content, while PS oil is mostly composed of higher aromatics. Influence of the plastic content on the selectivity of produced compounds from investigated mixtures is obvious. An only small portion of plastic in fuel mixture promotes the formation of compounds with higher carbon content reaching the maximum value for mixture with an equal share of both fractions. As the content of plastic increase in the mixture, homogeneity of oil is slightly reduced. Most probably, this is due to thermal decomposition of monomer styrene on toluene, various benzene-based compounds and PAHs [18]. This statement is in agreement with Table 6., where a notable reduction of styrene share is identified as the plastic content increase. For this reason, in Table 7., there can be seen the reduction of the share of identified compounds for mixture with 75% of PS regarding the C-content. It should be emphasised that there is no actual decrease of such compounds in obtained oil, but the oil has a more heterogeneous structure with a great number of species presented in traces or with a yield below 0.5%.

Table 7. - Yield of oxygenated and potentially harmful compounds

Investigated sample **Organic group**	**Bio-oil [%]**	**PS oil [%]**	**PS/SD 25-75% [%]**	**PS/SD 50-50% [%]**	**PS/SD 75-25% [%]**
Phenols	12.25		3.72	1.73	1.13
Ketones	16.16		<1.0%	<1.0%	<1.0%
PAHs/Furans	11.86	12.14	6.86	9.43	10.26
Alcohols	4.21				
Ethers/Acids	9.27				
Aldehydes	9.62				
Sugars	3.21				
Benzene-based	<1	12.67	13.48	16.24	16.62
C-content					
C_4-C_{12}	69.10	37.98	45.53	51.57	42.52
C_8-C_{16}	43.00	66.07	54.25	64.38	57.31
C_{24}		17.71	25.07	9.89	12.31

3.2.4. Gas product characterisation

The gaseous product can be considered as the by-products of pyrolysis, especially when the process is carried out on mild temperatures below 700°C, after which gasification takes place [7]. Therefore, characterisation of a gaseous fraction is interesting in terms to evaluate the potential of obtained syngas which could be utilised as an energy source for pyrolysis. From Fig. 4b) it is visible that for gas fraction synergistic effect is negative and gas yield is significantly lower compared to the theoretical yield. Dominant compounds for all investigated samples are carbon dioxide (CO_2) and carbon monoxide (CO). Valuable compounds preferred in syngas [46], like methane (CH_4) and hydrogen (H_2), are present with significantly lower share, while the share of higher hydrocarbons (C_xH_y) is almost negligible. Figure 5. presents the distribution of obtained syngas components within the temperature dependence. Highest generation of valuable gases like H_2, CH_4, and C_xH_y is observed for pyrolysis of pure PS, which also express the lowest yield of CO_2 and CO. In general, syngas obtained from the co-pyrolysis of various blends have a similar composition as the gas fraction obtained from individual SD pyrolysis, which is expected since the PS, has a meagre gas yield. The CO_2 and CO are the predominant components of syngas obtained from SD and mixtures pyrolysis, and they account for about 80% of volume share [47]. Remaining is equally divided between H_2 and CH_4, while the yield of higher hydrocarbons is below 2%. As expected, temperature increment favours the yield of syngas components as a result of secondary oil cracking [48]. Even though the PS has small influence regarding the gas product yield and distribution, its influence is still visible from figure Fig 5. b) and c). Addition of PS to fuel mixture lowered the temperature where the release of CO and CO_2 is noticed, suggesting that the introduction of plastic and interaction with biomass feedstock lowers the temperature where the decomposition mechanism starts. This is a valuable information for process optimisation, indicating that retention time and final temperature should be carefully selected to favour oil yield. It is interesting to notice that for all samples retaining the temperature at 600°C, promotes the formation of H_2 on the expense of CH_4 and higher hydrocarbons. This implies that longer retention time supports the secondary cracking of hydrocarbons to favour the yield of hydrogen, already reported by Singh et al. [49].

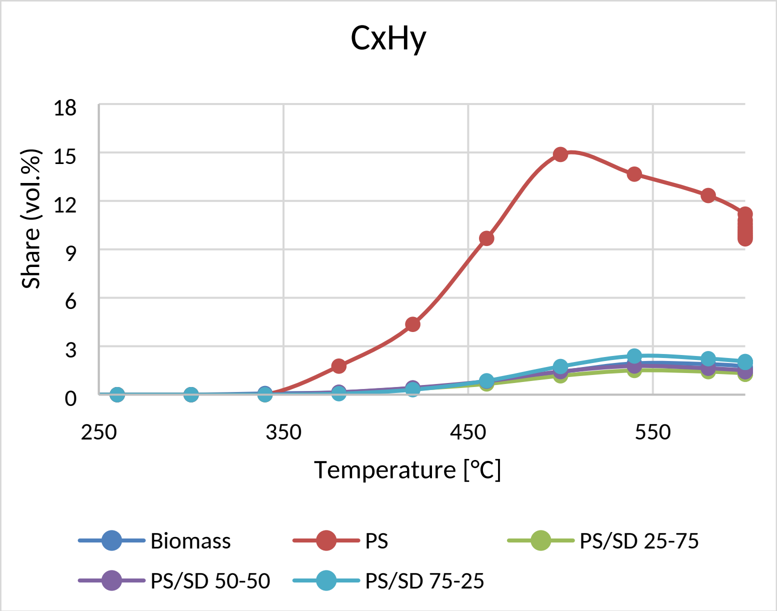


a)

b)

c)

d)



e)

Figure 5.- Distribution of gaseous products for all investigated samples

For obtained syngas composition, high heating values are calculated using Equation 3, where HHV_i presents the higher heating value of each gas component in MJ/m^3, and φ_i stands for volume share (vol.%) of respective component [20].

$$HHV = \sum \frac{HHVi * \varphi i}{100} \; [MJ/m^3] \tag{3}$$

Higher heating values (HHV) are calculated for all investigated temperatures, and the results are given in Figure 6. Highest heating value is ~11.5 MJ/m^3, calculated for the blend with PS/SD 75-25%. In general, HHVs at 600°C are between 10-11 MJ/m^3, while only PS exhibits values above 20 MJ/m^3; nevertheless, its yield is almost negligible (<1%).

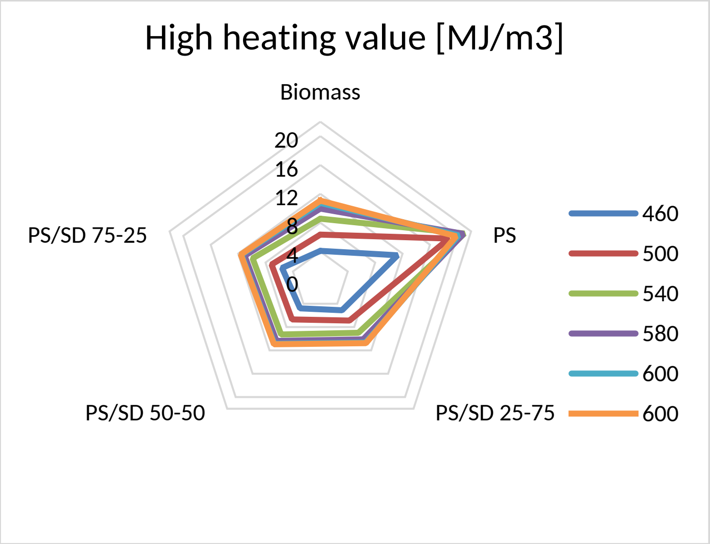
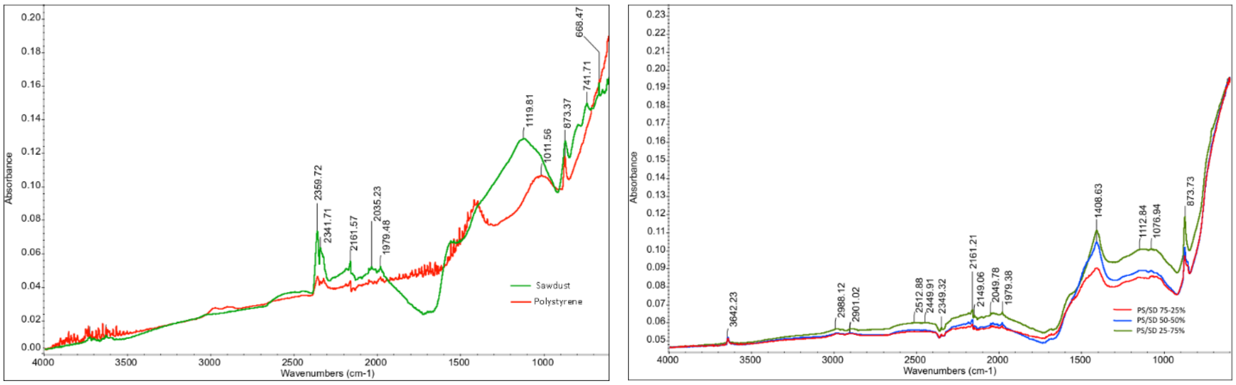


Figure 6. - Calculated HHV for obtained syngas compositions

3.2.5. *Char characterisation*

Char characterisation was done by FTIR analysis. Figure 7. shows the FTIR spectra for individual samples a), and respective fuel blends b). Intensive stretching in the range above 3500 cm^{-1} for PS is due to the high aromatics content. At 2341 and 2359 cm^{-1} it is observed intense stretch of the carbonyl group (C=O) for biomass, while the stretching in the range between 2035-2161 cm^{-1} corresponds to C-O group. Intensive peaks are noticed for PS between 1400-1700 cm^{-1}, which should correspond to the skeletal aromatic vibrations (C-H). Below 1000 cm^{-1}, C-H stretching of aromatics is notified for both samples [50].



a) b)

Figure 7. - FTIR spectra of char from a) individual pyrolysis, and b) respective blends

FTIR spectra obtained from co-pyrolysis of fuel blends express excellent matching. Stretching at 3643 cm^{-1} corresponds to the stretching of both alcohols and aromatics groups. Small peaks below 3000 cm^{-1} probably come from stretching in phenols and alcohols which are biomass products. The intensive peak is observed at 2348 cm^{-1}, which represents the stretching of carbonyl group from biomass and evolution of CO_2. At around 2161 cm^{-1} stretching of C-O is noticed which corresponds to the evolution of CO. The most intensive peak is observed at 1408 cm^{-1} for all blends, especially those with higher SD content which implies cellulose deformation. Once again, a sharp peak is noticed for 873 cm^{-1} which presents the styrene compound. Below 800 cm^{-1} stretching of higher hydrocarbons and C-H group is observed for all blends.

4. CONCLUSION

Co-pyrolysis of biomass sawdust and PS was carried out in a fixed-bed reactor with an aim to produce oil fraction and investigate the influence of plastic content on product quality. Results showed that PS significantly improve the yield of liquid fraction in both terms, quantity and quality. Only 25% of PS in mixture doubled the yield of bio-oil from 31 to 62%, simultaneously reducing the yield of oxygenated compounds characteristics for conventional bio-oils and promoting the formation of valuable aromatic hydrocarbons. Additionally, co-pyrolysis reduced the yield of harmful PAHs, especially visible for mixture with 25% of PS. Further increment of PS in the fuel mixture, reduced the yield of oxygenated compounds, nevertheless higher generation of unwanted benzene-based compounds and toxic PAHs is noticed as well. This is most probably result of a secondary cracking of monomer styrene which was obviously promoted by the interaction with biomass feedstock. Moreover, this resulted with the reduced homogeneity of obtained oil, since it was noted a significant increase in yield of various compounds presented in traces or with share below 0.5%. This information calls for cautious approach and more in-depth analysis regarding the optimal plastic content in fuel mixture.

Even though aromatic hydrocarbons have great calorific value, their share in commercial fuel is restricted to a maximum 40% since their combustion release smoke and toxic species. This indicates that PS might be a great solution to improve the oil yield and prevail the need for aromatic selective catalyst, but its share in mixtures should be limited. Since 25% of PS in fuel mixtures greatly improved the bio-oils properties, and further increment leads to several unwanted side-effects, this share could be considered optimal. For further work, it might be interesting to introduce the polypropylene (PP) in fuel mixtures with sawdust and PS. This is due to the fact that PP degrades in similar temperature range as PS, while mainly decompose on aliphatic hydrocarbons which are more appropriate in fuel mixtures then aromatics. Therefore, co-pyrolysis of sawdust, PS and PP could yield an optimal share of hydrocarbons that could meet fuel standards and specifications. Besides, fast pyrolysis with lower final temperature, shorter retention time and usage of appropriate catalyst could additionally improve the yield and properties of derived bio-oils, reducing the need for after-treatment methods and broadening application possibilities.

ACKNOWLEDGEMENT

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